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13. ABSTRACT (Maximum 200 words)

This research addressed the need for basic information concerning halogen etching of III-V semiconductors. The reactions of halogens with semiconductor surfaces are the fundamental chemical interactions in processes employed for device manufacture. In this work, the reactions of XeF₂, Cl₂ and I₂ with III-V semiconductor surfaces were investigated with synchrotron-based soft x-ray photoelectron spectroscopy, low energy electron diffraction and scanning tunneling microscopy. Fluorine reaction grows films of group III fluorides, which can be used as dielectric materials. Chlorine is the most widely used halogen for dry etching, while iodine has been proposed for use as a "gentle" etchant. We found that, for all of the halogen reactions, the initial adsorption depends on the surface reconstruction, stoichiometry and condition. Some surfaces passivate, while others spontaneously etch at room temperature. The passivated surfaces are well-ordered and covered with approximately one monolayer of adsorbed halogen. The etched surfaces, on the other and, are considerably rough and atomically disordered. A microscopic model is proposed which assumes that halogen atoms preferentially adsorb onto a group III atom if the surface is initially well-ordered. Further reaction depends on the ability of higher halides to form on the surface. This microscopic model can explain why certain surfaces etch, while others form ordered overlayers.

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Sincerely,
Jory A. Yarmoff

FINAL TECHNICAL REPORT

A. STATEMENT OF THE PROBLEM STUDIED

This research addressed the need for fundamental information concerning halogen etching of III-V semiconductors. The chemical reaction of atomic and molecular halogens with semiconductor surfaces is the major component of most dry processes employed for device manufacture. Processes such as reactive ion etching and chemical vapor deposition are most often optimized by empirically balancing requirements for smooth surfaces and high etch rates, with little knowledge of the surface chemistry on the microscopic scale. By providing a fundamental understanding of the relevant surface chemistry, it will be possible to optimize current processes and to design new ones in a more efficient manner. The information obtained from this research is also critical for the development of new types of processes, such as atomic layer epitaxy (ALE), that are designed to produce atomic-scale structures.

We carried out experimental investigations of the reactions of XeF_2 [1-2], Cl_2 [6-8, 10], and I_2 [3-5, 11] with particular III-V semiconductor surfaces. The research made use of the tools of surface science to investigate fundamental aspects of a "real" technological problem. We used synchrotron-based soft x-ray photoelectron spectroscopy (SXPS, collected at the National Synchrotron Light Source at Brookhaven National Laboratory), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) to measure the surface products formed by reaction under well-controlled conditions. During this time, we also wrote a review article [9] that reported on the current state of the field. We showed how many techniques can be used together to solve such surface chemical problems. From these many results, an atomic-level understanding of halogen/III-V semiconductor reactions is emerging.

B. SUMMARY OF THE MOST IMPORTANT RESULTS

Fluorine is not normally used as an etchant for III-V materials, due to the involatility of group III metal fluorides. The reaction does have microelectronics applications, however, as it can be used to grow films of group III fluorides for use as dielectric materials. The room temperature reaction of XeF_2 with GaAs produces films of solid GaF_3 , which is a 10 eV bandgap insulator, while the excess As is removed from the surface. We investigated the evolution of the insulator/semiconductor interface with film growth [1] and the effects of surface temperature on the reaction [2]. It was found that the interface region between the GaF_3 film and the substrate consists of GaF, AsF and tri-coordinate Ga and As atoms. Group III and V elements are stable in tri-coordinate configurations, which form as bonds break in the near-surface region. The size and composition of the interface region is independent of the film thickness. Measurements of samples that were reacted with XeF_2 at ~ 600 K, which is above the decomposition temperature of GaF_3 , showed that Ga and As are removed stoichiometrically, while a thin film (~ 1 atomic layer) of elemental As remains on the surface [2]. These results indicate that the interaction of fluorine with GaAs is a frustrated etching reaction, which is a consequence of the low volatility of Ga fluorides.

Chlorine is the halogen most widely used in device manufacture. Cl_2 adsorbs dissociatively on III-V semiconductor surfaces, and can spontaneously etch the substrate under certain conditions. For reaction with GaAs, we investigated the effects of the initial surface structure [7], substrate temperature [6], and exposure level [8]. The adsorption pathway is dependent on the clean surface reconstruction and condition [7]. Ga-rich surfaces are initially more reactive than As-rich surfaces. The initial adsorption kinetics are described by the Elovich equation, i.e., the sticking coefficient for Cl_2 decays exponentially with the amount of adsorbed Cl.

Although GaAs surfaces appear to passivate after the initial exposures to Cl_2 at room temperature, they begin to etch after larger exposures. In the early stages of etching, Ga is preferentially

removed from the surface. The etching reaction ultimately produces volatile AsCl_3 and GaCl_3 , which form through the stepwise addition of Cl. After sufficient Cl_2 exposure to attain steady-state etching, the surfaces are terminated by $-\text{AsCl}-\text{GaCl}_2$ "tree"-like structures. The surfaces are very rough and contain buried tri-coordinate atoms, in a similar manner as the interfaces produced by fluorine reaction. Such "tree" structures, and the associated disorder, are likely to be involved in Cl_2 reactions with other III-V surfaces, as well. The addition of the final Cl atom in forming gaseous GaCl_3 was identified as the rate-limiting step in the overall etching reaction.

There is a correspondence between the gas phase and surface products formed at different temperatures, which allows for the microscopic reaction mechanism to be modeled. At low temperatures, the gaseous products are the tri-chlorides and the surface products are the intermediate mono- and di-chlorides. At higher temperatures, the gaseous products are GaCl and As dimers and tetramers. Accordingly, we found that at temperatures between 500 and 600 K, the surfaces are etched by Cl_2 and the resultant surface layer is composed of elemental As and contains no chlorine [6], similar to the high temperature fluorine reaction. For reaction at temperatures above 600 K, stoichiometric etching is observed, which produces clean GaAs surfaces with a very high degree of crystallinity. Reaction with Cl_2 at elevated temperature therefore provides a new method whereby clean, well-characterized and well-ordered GaAs surfaces can be reproducibly prepared without the need for complex procedures, such as molecular beam epitaxy (MBE).

For the reaction of Cl_2 with InAs(001), we compared adsorption on the In-terminated $c(8 \times 2)$ surface to that of the As-terminated $c(2 \times 8)$ structure [10]. Although the largest reaction occurs with the element that terminates the surface, Cl_2 does in fact react with both elements. From this, we conclude that the reaction is very similar to that of Cl_2 with GaAs, in that (1) substrate bonds are broken, i.e., etching can occur at room temperature, and (2) the details of the reaction depend on the initial surface stoichiometry.

Iodine can also etch III-V semiconductors, and has been proposed for use as a more "gentle" etchant than chlorine. We investigated the reaction of I_2 with GaAs, InAs and InSb (001) surfaces. For low exposures at room temperature, I_2 forms very highly ordered 1×1 structures [3-5]. We investigated the dispersion of the surface electronic states of these structures [5], the chemical reactions of I_2 with the substrates [3], and the order within the iodine overlayers [4]. The ordered structures involve minimal disruption of the substrate, as iodine simply bonds to the outermost surface atoms. The 1×1 ordered overlayers have a state located at ~ 4.4 eV below the valence band maximum, which shows a dispersion within a 1×1 surface Brillouin zone, and passes through an open lens in the projected bulk density of states [5]. Both I 4d SXPS spectra and STM images collected from the ordered surfaces show two types of iodine, which may be related to iodine bound to broken and unbroken surface dimer atoms [4]. When the iodine-covered surfaces are annealed, the group III element is preferentially etched, producing a group V-terminated surface. This result thus suggests a means whereby a single atomic layer can be removed via a surface chemical reaction. This "atomic layer etching" process can be exploited to produce certain surface structures that previously required the use of MBE.

It has been observed that some III-V surfaces spontaneously etch upon adsorption, while others form ordered overlayers. A careful study, in which we compared I_2 reaction with two different InAs(001) reconstructions, has lead to a microscopic model of halogen/III-V reactions [11]. The utility of this experiment was that a single material could be prepared so that it either passivated or etched, depending on the details of the structure. We found that on the In-terminated $c(8 \times 2)$ surface, a sharp 1×1 LEED pattern formed following I_2 exposure, indicating that the surface was highly-ordered. SXPS indicated that all of the iodine was singly coordinated to surface In atoms, i.e., none was bonded to As. On the As-terminated $c(2 \times 8)$ surface, on the other hand, the surface became highly disordered by the reaction, and iodine was bonded to both In and As.

The microscopic model that explains these observations is based on the assumption that iodine will preferentially react with surface group III (i.e., In) atoms, as opposed to group V elements. On the well-ordered clean surface, the group III atoms have an empty orbital extending into the vacuum, while the group V atoms have a filled orbital, i.e., a lone pair of electrons. There will be some repulsion between the lone pair of a group V atom and the valence electrons of the incoming I_2 , while there will be attraction between the unoccupied orbital of a group III atom and the I_2 molecule. For the In-terminated surface, reaction therefore occurs with the outermost atoms and the structure remains well-ordered. On the group V-terminated surface, however, the reaction most likely occurs at a group V element located in the second layer in one of the missing rows. When an iodine bond is formed with a second layer atom, it withdraws charge from the first layer group V atom. This depletes the surface lone pair, thereby making the outermost group V more reactive to I_2 . Thus, after sufficient reaction to observe iodine bonding with SXPS, I is attached to both In and As. This scenario enables substrate bonds to weaken and to then break, which ultimately leads to etching. Thus, this microscopic model can explain why halogen reaction produces an ordered overlayer with some surfaces, while other surfaces become disordered and etch.

In summary, an experimental program probing the basic surface chemical reactions of halogens with III-V semiconductor surfaces has been completed. Much has been learned about the surface chemical products formed, the kinetics of the reactions, and the structures of the resulting surfaces. In addition, we learned how to exploit these reactions for the production of novel surface structures. Finally, a microscopic understanding of these reactions has begun to form.

C. LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS

1. W.C. Simpson, T.D. Durbin, P.R. Varekamp and J.A. Yarmoff, "The Growth of GaF₃ Films on GaAs(110) at Elevated Temperatures Studied with Soft X-ray Photoelectron Spectroscopy", *J. Appl. Phys.* **77**, 2751-2758 (1995).
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8. W.C. Simpson, D.K. Shuh and J.A. Yarmoff, "Room Temperature Chlorination of As-Rich GaAs(110)", *J. Vac. Sci. Technol. B* **14**, 2909-2913 (1996).
9. W.C. Simpson and J.A. Yarmoff, "Fundamental Studies of Halogen Reactions with III-V Semiconductor Surfaces", *Ann. Rev. Phys. Chem.* **47**, 527-554 (1996).
10. W.K. Wang, W.C. Simpson and J.A. Yarmoff, "Photoemission Studies of the Chemisorption of Cl₂ on InAs(001)", National Synchrotron Light Source Annual Report 1997 (one page).
11. W.K. Wang, W.C. Simpson and J.A. Yarmoff, "Passivation versus etching: Adsorption of I₂ on InAs(001)", *Phys. Rev. Lett.* **81**, 1465-1468 (1998).

D. PARTICIPATING SCIENTIFIC PERSONNEL

<u>Name</u>	<u>Position</u>	<u>Degree awarded</u>
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Wei K. Wang	Graduate Student	Ph.D. awarded 8/00